Nucleation and Growth of Cetyl Trimethyl Ammonium Bromide Micelles at the Interphase $Hg/NaCl_{(aq)}$ 0.1M.

V. M. Vital-Vaquier¹, M. T. Ramírez-Silva^{1,*}, M. Romero Romo² and M. Palomar Pardavé²
1 Universidad Autónoma Metropolitana-Iztapalapa.
Depto. de Química, Área de Química Analítica, Apdo. 55-534, C.P. 09340, México D.F., México.
2 Universidad Autónoma Metropolitana-Azcapotzalco.
Depto. de Materiales, Área de Ciencia de los Materiales, C.P. 02200. México D.F. México

Corresponding author e-mail: mtrs218@xanum.uam.mx

Introduction. Presently, the adsorption of anionic or cationic surfactants on various interphases has created considerable interest. Such systems relate to numerous practical situations, like mineral flotation, lubrication, metal electrodeposition and stabilization of colloidal solutions [1-3]. There are also negative impacts on several ecosystems: accumulation increases contamination, and in extreme cases, they may destroy marine environments [4].

Surfactant adsorption processes involve 2D film formation, even at a concentration below the critical micelar concentration, CMC. Analysis of capacitance-potential curves [5], and direct observation of the surfaces by means of STM [6-7] and AFM corroborated this. Cationic surfac-tants such as CTAB have been less studied; they favour electron transfer amidst anionic radicals and organic substrates difficult to oxidize. In this work, we present the results of the electrochemical study on the adsorption of CTAB over Hg, mainly using the potentiostatic technique [6-8].

Experimental. Reagent grade reactants were used to prepare aqueous solutions with various CTAB concentrations. Room temperature measurements of electrocapillarity, voltammetry, AC and cyclic and potentiostatic current transients were carried out using a BAS 100W potentiostat, software controlled, using high purity dripping mercury as working electrode, Pt as auxiliary and Ag/AgCl as reference.

Results. Nearly parabolic electrocapillarity curves were obtained for different CTAB concentrations in NaCl 0.1 M solutions, which present maxima at about -0.5 V. The magnitude of the surface tension decreased as the CTAB concentration increased. The shape of the curves was modified by the surfactant, imposing a tendency to widen the maxima into potential intervals; the surface tension is beginning to appear independent of the applied potential.

The potentiostatic current transients, i-t curves for a CTAB solution $6.66 \times 10^{-5} \text{M}$ showed an exponential current drop that decreases in rate as time increases, thus indicating that the double layer charge process is occurring, however these curves also present, a common feature, different from the pure capacitor charge process, related to surfactant adsorption on the metallic surface of the electrode. The results from AFM indicate that a 2D film is formed on the mercury electrode surface in the CTAB containing solution. Therefore, in this work we propose that the kinetics for this formation process can be described by the expression: $I(t) = I_{DL} + I_{2Di-li}$, where I_{Dl} is the current due to the double layer charge process and I_{2Di-li} is the contribution associated with a 2D nucleation

process. In Fig. 1, a comparison of an experimental current transient obtained upon adding CTAB to the solution, and a theoretical transient obtained by non-linear fitting of experimental data in the equation above.

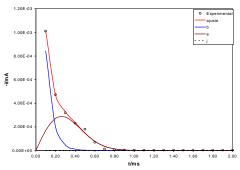


Fig. 1. Comparison between an experimental transient (O) obtained in the system Hg/6.66x10⁻⁵M CTAB, 0.1M NaCl, at an applied potential of -0.85 V, with a theoretical transient (red) as obtained by non-linear fitting of experimental data in equation (6). Individual contributions due to the double layer charge (blue) and the 2D nucleation process (black) are also shown

The equation fitting is quite adequate, though it does not suffice to fully accept the mathematical model to represent the physical process occurring. In this work, we show that the fitting parameters actually have physical meaning.

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